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U.S. GEOLOGICAL SURVEY

**Water-Quality Data for Selected National
Park Units, Southern and Central Arizona
and West-Central New Mexico,
Water Years 2003 and 2004**

Open-File Report 2005–1291

Prepared in cooperation with the NATIONAL PARK SERVICE

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By James G. Brown

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**U.S. Department of the Interior
U.S. Geological Survey**

U.S. Department of the Interior

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Conversion Factors and Datum

| Multiply | By | To obtain |
|--|----------|--|
| Length | | |
| inch (in.) | 2.54 | centimeter (cm) |
| inch (in.) | 25.4 | millimeter (mm) |
| foot (ft) | 0.3048 | meter (m) |
| mile (mi) | 1.609 | kilometer (km) |
| mile, nautical (nmi) | 1.852 | kilometer (km) |
| Area | | |
| square mile (mi ²) | 2.590 | square kilometer (km ²) |
| Volume | | |
| acre-foot (acre-ft) | 0.001233 | cubic hectometer (hm ³) |
| Flow rate | | |
| cubic foot per second (ft ³ /s) | 0.02832 | cubic meter per second (m ³ /s) |
| gallon per minute (gal/min) | 0.06309 | liter per second (L/s) |
| gallon per day (gal/d) | 0.003785 | cubic meter per day (m ³ /d) |

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Elevation, as used in this report, refers to distance above the vertical datum.

Water-Quality Data for Selected National Park Units, Southern and Central Arizona and West-Central New Mexico, Water Years 2003 and 2004

By James G. Brown

Abstract

In 1992 the National Park Service began a Level 1 Water Quality Data Inventory program to make available to park managers the water-resource information with which to best manage each park and plan for the future. Scientists at the U.S. Geological Survey Arizona Water Science Center in Tucson, Arizona, collected water samples and other water-quality information at 30 sites in 9 park units in southern and central Arizona and west-central New Mexico in water years 2003 and 2004. Sites consisted of springs, seeps, mine adits, streams, and wells. The baseline water-quality data presented in this report were determined through field measurements and laboratory analyses of selected physical properties and chemical constituents. Field measurements made at each site were pH, specific conductance, water temperature, dissolved-oxygen concentration, and alkalinity. Water samples collected at each site were submitted to the U.S. Geological Survey National Water Quality Laboratory and analyzed for major-ion, trace-element, and nutrient concentrations. Analyses done at selected sites included turbidity, coliform counts, and concentrations of suspended sediment, turbidity, cyanide, and arsenic. Quality control for this study was maintained through the use of proper training, use of standard field and laboratory protocols, collection of sample blanks and replicates, and thorough review of the analytical results. Laboratory analyses were done using methods approved by the U.S. Geological Survey or the U.S. Environmental Protection Agency.

Measured field pH values ranged from 6.4 to 9.2, within the normal range expected for springs and rivers. Dissolved-solids concentrations ranged from 49 to 1,570 milligrams per liter; most values were less than 700 milligrams per liter. Dissolved-solids concentrations of less than 100 milligrams per liter were almost always associated with springs at altitudes higher than 7,000 feet in the Rincon Mountain District of Saguaro National Park. Trace-metal concentrations at most sites were at or near laboratory reporting levels. The highest metals concentrations were at Blue Waterfall Seep below an unnamed mine in Coronado National Memorial where concentrations of dissolved copper were as high as 505 micrograms per liter. Concentrations of dissolved zinc

were as high as 3,650 micrograms per liter at Blue Waterfall Seep below an unnamed mine and 1,530 micrograms per liter at Barrel Springs windmill.

Concentrations of dissolved arsenic were measured in water samples from the Middle and West Forks of the Gila River in the Gila Cliff Dwellings National Monument and ranged from 0.5 to 1.6 micrograms per liter. Not including sites in Coronado National Memorial, most concentrations of dissolved uranium were less than 10 micrograms per liter. At one site in Coronado National Memorial concentrations were as high as 122 micrograms per liter. Fecal coliform bacteria colony counts were made at 12 sites to indicate the possible presence of contamination from human or animal wastes. Samples were collected twice at nine sites and once and three sites. Colony counts ranged from 0 colonies per 100 milliliters at two sites to 660 colonies per 100 milliliters at Beaver Creek in Montezuma Castle National Monument. At sites where more than one analysis was done, colony counts varied significantly from visit to visit. For example, colony counts at Yaqui Spring were 28 colonies per 100 milliliters in May 2003 and 0 colonies per 100 milliliters in September 2003. The highest nutrient concentrations were found at Wild Horse Mine in the Tucson Mountain District of Saguaro National Park, where nitrate concentrations were as high as 92 milligrams per liter.

Introduction

In 1992 the National Park Service (NPS) began the Level 1 Water Quality Inventory Program, a cooperative undertaking designed to characterize baseline water quality in park units throughout the United States. The goal of the project is to make available to park managers the water-resource information with which to best manage each park and plan for the future. As part of this program, scientists at the USGS Arizona Water Science Center in Tucson, Arizona, collected water samples and other water quality information at 30 sites in 9 park units in southern and central Arizona and west-central New Mexico (fig. 1 and table 1) in water years 2003 and 2004. An attempt was made to collect samples

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three times at each site during the course of the study. Sample locations included springs, seeps, mine adits, streams, and wells. The nine NPS units at which samples were collected vary greatly in terms of physiographic climatic characteristics (table 2).

Purpose and Scope

The purpose of this report is to present the results of baseline water-quality sampling done during water years 2003 and 2004 of 30 key water bodies at selected national park units

in the Sonoran Desert Network of the NPS (table 1). The nine park units from which samples were obtained ranged in size from 360 to 330,000 acres. The Sonoran Desert Network is mainly in the Sonoran Desert and Mexican Highland sections of the Basin and Range Physiographic Province defined by Fenneman (1931). Rainfall in most of the province ranges from less than 8 to 16 inches per year, but may exceed 36 inches at high altitudes in mountainous regions (Western Regional Climate Center, 1997). Rainfall in the province occurs in a bimodal pattern that consists of frontal storms that occur during the winter, and thunderstorms that occur during the summer monsoon season.



Figure 1. National park units at which ground-water and surface-water samples were collected, water years 2003 and 2004.

Site Selection and Sampling

A total of 30 sites in Arizona and New Mexico were sampled from 9 units in the Sonoran Desert Network of the NPS (table 1). Sampling locations were selected in consultation with NPS personnel to ensure that key water bodies in each of the park units were included. Key water bodies are those that are essential to the cultural, historical, or resource themes of a particular unit, or provide habitat for threatened or endangered plants and animals. Initial plans called for 3 samples to be collected at each site during the study to describe any possible seasonal variations in water quality. Only 24 sites were sampled 3 times owing to drought conditions and lack of water during parts of each year. Samples were collected twice at 3 sites, and once at 3 sites.

Methods and Protocols

The baseline water-quality data presented in this report were determined through field measurements and laboratory analyses of selected physical properties and chemical constituents. The measurements and analyses to be done at each site were determined collaboratively by NPS and USGS scientists to meet the requirements of the NPS Level 1 Water Quality Inventory Program. Field measurements made at each site were pH, specific conductance, water temperature, dissolved-oxygen concentration, and alkalinity. Water samples collected at each site were submitted to the USGS National Water Quality Laboratory (NWQL) and analyzed for major-ion, trace-element, and nutrient concentrations. Additional analyses or measurements were done at selected sites on the basis of local geologic conditions, past water-quality analyses, and nearby historical or ongoing human activities that were perceived to pose specific threats to water quality. Measurements or analyses done at selected sites included turbidity, coliform counts, and concentrations of cyanide and arsenic.

Field measurements were done in accordance with standard USGS protocols, which are documented in the National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Alkalinity was measured in the field either by gran or incremental titration. Nutrient, major ion, trace element, arsenic, and alkalinity samples were filtered through a 0.45-micron pore size filter. Samples were preserved as required by sampling and analytical protocols. Laboratory analyses were done at the NWQL by methods documented in the following publications: Fishman and Friedman (1989), Faires (1993), Fishman (1993), McLain (1993), Struzeski and others (1996), American Public Health Association (1998), and Garbarino (1999).

Quality Control

Quality control for this study was maintained through the use of proper training of field personnel, use of standard field and lab protocols, collection of sample blanks and replicates, and thorough review of the analytical results. At least one USGS scientist in each field crew was a participant in the USGS National Field Quality Assurance Program, which requires the successful determination of pH, specific conductance, and alkalinity in reference samples supplied by the USGS Branch of Quality Systems (BQS). Field crews also were trained in other aspects of water-quality sampling either through formal courses offered by the USGS or individual instruction from USGS personnel experienced in water-quality data collection activities.

Laboratory analyses were done at NWQL using methods approved by the USGS or the U.S. Environmental Protection Agency (USEPA). Internally, the USGS BQS audits the NWQL to assure that procedures comply with USGS standards. Externally, the NWQL is certified by the USEPA drinking water program to analyze drinking water samples. In addition, the USGS has taken part in the USEPA National Environmental Laboratory Accreditation Program since 1995 and has redesigned its quality systems to meet standards developed by the National Environmental Laboratory Accreditation Conference. Major cations and anions were analyzed by using a combination of chromatographic and spectrometric methods. Most trace elements were determined by using inductively-coupled plasma mass spectrometry. Nutrients were analyzed by using colorimetric methods. The detection level used by the NWQL for most analytes is the laboratory reporting level (LRL) (Childress and others, 1999). This reporting level is determined through a statistical procedure designed to yield a false positive rate of less than one percent at the LRL (USGS, 1999), and is twice the long-term method detection level.

During the first sampling round of the study, five field blanks were taken to assure that the methods and sampling procedures used would yield environmental samples that were free from contamination. Analysis of the field blanks indicated no major problems with the methods, though several trace metals were detected in two of the samples, albeit at low levels. Aluminum was detected in two out of the five blanks, at concentrations of 2 $\mu\text{g/L}$ (the laboratory reporting level) and 5 $\mu\text{g/L}$ (table 3). Concentrations of dissolved aluminum in the environmental samples ranged from less than 2 $\mu\text{g/L}$ to 54 $\mu\text{g/L}$. Measured environmental concentrations of dissolved aluminum in the same order of magnitude as blank detection concentrations should be viewed with caution. Several major ions were also detected in the field blanks, but at concentrations one to two orders of magnitude lower than those measured in the environmental samples (table 4).

Replicate samples were collected at five sites to estimate the variability in the sampling and analytical processes. For small data sets, quality control replicates are especially

important in evaluating the results of a sampling program. For most sample pairs (replicate and environmental analyses of a particular analyte) in this study, concentrations in replicate samples were within 5 percent of concentrations in the environmental samples. For the major ions, the difference exceeded 5 percent in 4 out of 35 sample pairs (7 analytes at 5 sites), and 10 percent in 1 sample pair. Percentages were calculated by dividing the difference by the average of the environmental and replicate values. The maximum difference was for the potassium analysis of the sample from the State of Texas Seep, for which the replicate and environmental results differed by 16 percent. One suspended-sediment replicate was collected (at Beaver Creek); the concentration in the replicate differed by 86 percent from the concentration in the environmental sample.

In terms of maximum percent differences, greater variability was observed in the minor-ion (iron and manganese) and trace-element analyses than in the major-ion analyses. As was the case with the latter, most minor-ion and trace-element replicate and environmental analyses agreed within 5 percent. Differences were greater than 5 percent in 9 out of 105 sample pairs and greater than 10 percent in 8 out of 105 sample pairs. For all but one analyte, no more than 1 out of the 5 sample pairs differed by more than 5 percent. The one exception was for manganese, for which 3 out of 5 sample pairs differed by more than 5 percent and 2 out of 5 sample pairs differed by more than 10 percent. For the trace elements, variability was greatest at or near laboratory reporting levels, where differences were as great as 67 percent. For the nutrient analyses, differences between replicate and environmental values were within 5 percent.

Water-Quality Data

The results of the sampling done for this study provide baseline information on water chemistry and quality that facilitate the better management of scarce water resources in park units in the Sonoran Desert network of the NPS. The concentrations of dissolved constituents at the sites sampled for this study were compared to USEPA primary and secondary maximum contaminant levels (MCLs and SMCLs, respectively) (U.S. Environmental Protection Agency, 2003). It should be noted, however, that these MCLs were written for public water systems, and exceedances at the sites sampled for this study do not necessarily render them unsuitable for their respective uses (table 1). In addition, secondary levels are non-enforceable limits related to taste or other aesthetic characteristics that relate mainly to drinking water.

Measured field pH values ranged from 6.4 to 9.2, within the normal range expected for springs and rivers (Hem, 1985). Measured pH values of at least 9.0 were measured at three sites, all of which were in the Rincon Mountain District of Saguaro National Park. Values at these three sites varied with time, however, and pH was 9.0 or greater on only one of three

visits made to each site. Measured pH at Chimenea Creek, for example, was 9.2 in November 2002, 7.2 in April 2003, and 7.9 in October 2003 (table 4). The upper USEPA SMCL for pH of 8.5 was exceeded at Beaver Creek in Montezuma Castle National Monument, and at 5 sites in Saguaro National Park (table 4).

All samples collected for this study were analyzed for dissolved concentrations of major and minor cations and anions present in the water. The major-ion composition is in large part a reflection of the water-rock interactions that occur as water moves from a recharge area to the point at which it is sampled. At most sites the dominant cation was calcium and the dominant anion was bicarbonate. This was true for at least one site at almost every park unit sampled. At a few sites no one cation dominated. At two sites—Wild horse Mine in Saguaro National Park and Blue Waterfall Seep in Coronado National Memorial—sulfate was the dominant anion. The sulfate SMCL of 250 mg/L was exceeded at Wildhorse Mine, where concentrations of dissolved sulfate ranged from 456 to 495 mg/L. The secondary fluoride MCL of 2 mg/L was exceeded at Shake Spring. The SMCLs for iron and manganese were exceeded at 3 and 10 sites, respectively.

Dissolved-solids concentrations ranged from 49 to 1,570 mg/L. Most values, however, fell into a much narrower range. Out of a total of 82 samples, 73 yielded concentrations of less than 700 mg/L. The dissolved solids SMCL of 500 mg/L was exceeded at 5 sites. Concentrations of less than 100 mg/L were almost always associated with springs at altitudes higher than 7,000 ft in the Rincon Mountain District of Saguaro National Park.

Concentrations of suspended sediment were measured in streams at selected sites in the Gila Cliff Dwellings and Montezuma Castle National Monuments. Large concentrations are possible indicators of human activities, such as mining or agriculture, or natural phenomena, such as wildfires. Concentrations ranged from 3 to 131 mg/L; 9 out of the 12 analyses yielded concentrations of less than 20 mg/L. The largest concentrations were in Beaver and Wet Beaver Creeks in Montezuma Castle National Monument.

Trace-metal concentrations at most sites were at or near laboratory reporting levels. The highest concentrations were found at Blue Waterfall Seep below an unnamed mine in Coronado National Memorial. Concentrations of dissolved copper, for example, ranged from less than 0.2 µg/L to 9.6 µg/L at all sites except for Blue Waterfall Seep below an unnamed mine. Concentrations at this site were 377 µg/L and 505 µg/L in January 2003 and September 2003, respectively. The cadmium MCL of 5 µg/L was exceeded at Blue Waterfall Seep below an unnamed mine, where concentrations of were as high as 29 µg/L. With the exceptions of samples from Blue Waterfall Seep below an unnamed mine and Barrel Springs windmill in the Tucson Mountain District of Saguaro National Park, concentrations of dissolved zinc ranged from 0.6 to 38 µg/L, and most were less than 10 µg/L. Concentrations of

dissolved zinc were as high as 3,650 µg/L at Blue Waterfall Seep below an unnamed mine and 1,530 µg/L at Barrel Springs windmill.

Concentrations of dissolved arsenic were measured in water samples from the Middle and West Forks of the Gila River in the Gila Cliff Dwellings National Monument. High concentrations of arsenic can occur naturally under certain geologic conditions, but may also result from application of pesticides containing arsenic, or from mining activities (Hem, 1985). Measured concentrations of dissolved arsenic in the Middle and West Forks of the Gila River ranged from 0.5 to 1.6 µg/L. Samples were collected for cyanide analysis at the two springs sampled in Chiricahua National Monument. Elevated cyanide concentrations in water has been known to result from past or current mining activities. Concentrations of cyanide were less than the laboratory reporting level of 0.01 µg/L for all analyses.

All samples were analyzed for concentrations of dissolved uranium. The expected range of uranium in natural waters is 0.1 to 10 µg/L (Hem, 1985). Not including one site in Organ Pipe National Monument and several sites in Coronado National Memorial, concentrations ranged from 0.01 to 10.1 µg/L. At Williams Spring in Organ Pipe National Monument, the concentration of dissolved uranium was 32 µg/L in October, 2003, slightly above the USEPA MCL of 30 mg/L.

At sites in Coronado National Memorial, concentrations ranged from 0.01 to 122 µg/L. Concentrations exceeded 10 µg/L at seven out of eight sites sampled in the memorial. The USEPA uranium MCL was exceeded at the State of Texas Mine #11 and the Clark-Smith Mine. The highest concentrations were at the State of Texas Mine #11, where concentrations ranged from 113 to 122 µg/L.

Fecal coliform bacteria colony counts were made at 12 sites to indicate the possible presence of contamination from human or animal wastes. Samples were collected twice at nine sites and once at three sites. Colony counts ranged from 0 to 660 col/100mL. The USEPA fecal coliform MCL of 1 col/100 mls was exceeded at least once at 11 out of the 12 sites.

At sites where more than one analysis was done, colony counts varied significantly from visit to visit. For example, colony counts at Yaqui Spring were 28 col/100 mL in May 2003 and 0 col/100mL in September 2003. The largest colony counts were at sites in Montezuma Castle National Monument. At Beaver Creek, concentrations of fecal coliform were 4 col/100mL in May 2003 and 660 col/mL in September 2003. One site, Old Spring in Tumacacori National Historical Park, yielded counts of 0 col/100mL for both samples.

Nutrient concentrations were measured at all sites as possible indicators of human activities. Although various forms of dissolved nitrogen and phosphorus occur naturally in ground and surface waters, large concentrations may result from application of fertilizers, or from human or animal wastes (Hem, 1985). Measured concentrations of dissolved ammonia, nitrite, and nitrate were at or near laboratory

reporting levels at most sites. The USEPA nitrite MCL of 1 mg/L was exceeded only at Dripping Springs. Concentrations of dissolved nitrate ranged from 2.5 to 3.0 mg/L at Fern Grotto on Coronado National Memorial and 2.1 to 2.2 mg/L at Apache Spring in Fortt Bowie National Historic Site. Nitrate concentrations were as high as 8 mg/L at Dripping Springs in Organ Pipe Cactus National Monument. The USEPA nitrate MCL of 10 mg/L (as N) was exceeded at Wild Horse Mine in the Tucson Mountain District of Saguaro National Park. Measured concentrations at the mine ranged from 12 mg/L in March 2003 to 92 mg/L in August 2003. Measured concentrations of dissolved orthophosphate were at or near laboratory reporting levels at almost every site. The highest concentrations were found at Dripping Springs and Wild Horse Mine, where measured concentrations ranged from 1 to 4 mg/L.

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Water-Quality Data (available in Excel format)

Table 1. Level 1 water-quality sample sites.

Table 2. General site characteristics of national park units selected for level 1 sampling.

Table 3. Field Blank analytical results.

Table 4. Water-quality field measurements and laboratory analytical results for Level 1 sample sites in Southern and Central Arizona and West-Central New Mexico, Water Years 2003 and 2004.

Table 5. Field replicate analytical results.